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CUPRACARBORANES CONTAINING A CLOSO-CU(1)C2B9 GEOMETRY
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TECHNICAL REPORT NO. 128

Cupracarboranes Containing a *closo*-Cu(I)C₂B₉ Geometry.
Synthesis and Structure of [(PPh₃)CuC₂B₉H₁₁]⁺ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].

by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The reaction chemistry of $[nido-7,8-C_2B_9H_{11}]^{2-}$ with copper(I) has been examined to provide anaerobic synthetic routes to two novel phosphinocupracarboranes, $[(PPh_3)CuC_2B_9H_{11}]^-$ and $[(PPh_3)_2Cu_2(\mu-H)_2C_2B_9H_9]$. The structural analysis reveals that both cupracarboranes adopt a $closo$ geometry for the $d^{10}MC_2B_9$ icosahedra. Two copper(I) centers of the homodinuclear complex are incorporated into one carborane cage via the open pentagonal C_2B_3 face and two B-H-Cu bridges. Both bridging BH units stem from the upper pentagonal belt resulting in the interatomic Cu(I)-Cu(I) distance of 2.576(1) Å. The relatively close Cu(I)-Cu(I) proximity can be ascribed to a metal-metal interaction and the dinuclear cupracarborane can be viewed as a zwitterionic salt which upon dissolution remains intact while exhibiting fluxional behavior. The nature of these fluxional processes has been explored by variable temperature multinuclear FTNMR spectroscopy. <u>Key words: Crystallography</u> $[(PPh_3)_2Cu_2(\mu-H)_2C_2B_9H_9]$ crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.005(2)$, $b = 20.693(4)$, $c = 18.998(3)$ Å, $\beta = 92.664(6)^\circ$, $Z = 4$. $PPN[(PPh_3)CuC_2B_9H_{11}]^- \rightarrow$				
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crystallizes in the monoclinic space group $P2_1/n$, with $\underline{a} = 11.507(1)$, $\underline{b} = 14.772(1)$,
 $\underline{c} = 30.751(2)$ Å, $\beta = 90.284(2)^\circ$, $Z = 4$.

Cupracarboranes Containing a *closo*-Cu(I)C₂B₉ Geometry.

Synthesis and Structure of

[(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].



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Abstract

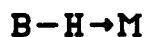
The reaction chemistry of [*nido*-7,8-C₂B₉H₁₁]²⁻ with copper(I) has been examined to provide anaerobic synthetic routes to two novel phosphinocupracarboranes, [(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉]. The structural analysis reveals that both cupracarboranes adopt a *closo* geometry for the d¹⁰ MC₂B₉ icosahedra. Two copper(I) centers of the homodinuclear complex are incorporated into one carborane cage via the open pentagonal C₂B₃ face and two B-H-Cu bridges. Both bridging BH units stem from the upper pentagonal belt resulting in the interatomic Cu(I)-Cu(I) distance of 2.576(1) Å. The relatively close Cu(I)-Cu(I) proximity can be ascribed to a metal-metal interaction and the dinuclear cupracarborane can be viewed as a zwitterionic salt which upon dissolution remains intact while exhibiting fluxional behavior. The nature of these fluxional processes has been explored by variable temperature multinuclei FTNMR spectroscopy.

[(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉] crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 10.005(2), *b* = 20.693(4), *c* = 18.998(3) Å, β = 92.664(6)°, *Z* = 4. PPN[(PPh₃)CuC₂B₉H₁₁] crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 11.507(1), *b* = 14.772(1), *c* = 30.751(2) Å, β = 90.284(2)°, *Z* = 4.

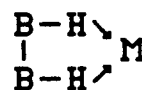
Cupracarboranes Containing a *closo*-Cu(I)C₂B₉ Geometry. Synthesis and Structure of [(PPh₃)CuC₂B₉H₁₁]⁺ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].

Sir:

An additional manifestation of the versatile electron donor ability of [*nido*-7,8-C₂B₉H₁₁]²⁻ (1) ¹ in metallacarborane chemistry has recently appeared in the form of polynuclear metallacarboranes involving exopolyhedral boron-hydride-metal three-center, two-electron linkages.^{2,3} While the bridge bonding mode I is the most usual pattern encountered in polynuclear metal complexes of 1, the unit II has only been realized in the bimetallic aluminacarborane, *commo*-3,3'-Al[(*exo*-8,9-(μ-H)₂Al(C₂H₅)₂-3,1,2-AlC₂B₉H₉)-(3',1',2'-AlC₂B₉H₁₁)] (2),^{3c,4} in which the bridging BH units stem from the upper and



I



II

lower pentagonal belts of one dicarbollide cage. As part of the investigation into the extended use of 1 in the synthesis of novel metallacarboranes containing metal-hydride-boron bridge bonds, the reaction chemistry of 1 with copper(I) has been examined.⁵

Routes to two novel phosphinocupracarboranes have recently been discovered. Depending on the absence or presence of (PPN)⁺Cl⁻ (PPN⁺ = *bis*(triphenylphosphoranylidene)ammonium cation), the dithallium salt⁶ of 1 reacts with triphenylphosphine-substituted

copper(I) chlorides (L_nCuCl , $n = 1,2$) to form either dinuclear *closo*-[*exo*-4,8-(μ -H) $_2Cu$ -(PPh $_3$)-3-(PPh $_3$)-3,1,2-Cu $_2$ B $_9$ H $_9$] (3; white; 79%) or mononuclear (PPN)[*closo*-3-(PPh $_3$)-3,1,2-Cu $_2$ B $_9$ H $_9$] [(PPN)-4; off-white; 84%]. Both compounds were characterized by single-crystal X-ray analyses⁷ as well as other means.⁸

The crystal structure of 3 consists of two enantiomers related by an inversion center to form the racemic system. The structure of 3, shown in Figure 1, contains two copper(I) centers

[Figure 1]

which are incorporated into one carborane cage via the open pentagonal C $_2$ B $_3$ face and two B-H-Cu bridges as in mode II. Both bridging BH units originate from the upper pentagonal belt, in contrast to 2, such that the plane of Cu(01)-B(04)-B(08) forms a dihedral angle of 40.9° with the pentagonal C $_2$ B $_3$ plane (± 0.016 Å) and the interatomic distance between two copper(I) ions of formal d¹⁰ configuration is 2.576(1) Å. This structural situation raises at least two engaging questions as to the geometry of the polyhedral framework of the Cu(03)C $_2$ B $_9$ fragment and the extent of Cu(I)-Cu(I) interaction.

The structure of metallacarboranes containing electron-rich late transition metal ions has been described in terms of molecular distortions such as the slipping,^{9,10} folding¹⁰ and tilting^{5,11} distortions. The parameters which are associated with these molecular distortions remain useful for descriptive purposes, but do not always delineate the electron count of the polyhedral framework of the MC $_2$ B $_9$ cages. Nevertheless, the structural analysis favors *closo* geometry for the Cu(03)C $_2$ B $_9$ cage of 3. In 3, the lower B $_5$ plane is nearly planar (± 0.004 Å) while the upper C $_2$ B $_3$ plane experiences a minor distortion with 2.3° and 1.1° for the folding parameters¹⁰ θ and ϕ , respectively. The displacement of Cu(03) from the perpendicular passing through the centroid of the lower B $_5$ plane, known as the slipping parameter Δ ,¹⁰ is calculated to be 0.25 Å. These values for the distortion parameters fall into the range observed in *closo* icosahedral metallacarboranes¹² rather than slipped metallacarboranes.¹³ The interaction of copper with the cage via the open C $_2$ B $_3$ face in 3 is typical of *closo*-MC $_2$ B $_9$ complexes so far

structurally characterized,^{14,15} with a mean M-C/M-B distance ratio (1.06) close to unity. The anionic *closo*-[LCuC₂B₉H₁₁]⁻ fragment of **3** can be synthesized as a separate, isolated entity. The compound (PPN)·**4** is such an example and the structure of **4**, as displayed in Figure 2, also

[Figure 2]

adopts *closo* geometry.¹⁶ The *closo* geometry for the d¹⁰ MC₂B₉ icosahedra, in both **3** and **4**, seems to be unusual since a progressive opening of the MC₂B₉ metallacarborane cage has been pointed out⁵ as a trend in the structural changes for the isoelectronic 18-electron series [Re(CO)₃-C₂B₉H₁₁]⁻,^{12a} [Au(S₂CNEt₂)C₂B₉H₁₁],^{11,13c} [Hg(PPh₃)C₂B₉H₁₁],^{5,17} and [Tl-C₂B₉H₁₁]⁻.^{17,18} However this geometry has been anticipated as a possible structure for (PPh₃)CuC₂B₉H₁₀(C₅H₅N)⁵ by analogy with the known η⁵ structure of (PPh₃)Cu(C₅H₅)¹⁹

A range of Cu-Cu distances from 2.35 Å to about 3.6 Å is found in polynuclear copper(I) compounds.²⁰ MO analyses performed with Cu_nⁿ⁺ (n = 2,4) at the extended Hückel level of approximation supports the existence of a soft and attractive Cu(I)-Cu(I) interaction, overlaid upon the requirements of the bridging ligand set.^{20b} In [Cu₂(tmen)₂(μ-CO)(μ-PhCO₂)]⁺ the bridging ligand stereochemistry dominates, resulting in the very short Cu(I)-Cu(I) distance of 2.419(2) Å,^{20c} whereas in **3** the stereochemical requirements of the bridging ligand (**1**) are likely to be minimal since the elevation angles of the hydrogen substituents in the MC₂B₉H₁₁ cages are not restricted to that of a regular icosahedron.^{10b} Thus the relatively close Cu(I)-Cu(I) proximity in **3** can be considered to be a consequence of a metal-metal interaction similar to that found in Fe₂(CO)₆C₄(CH₃)₂(OH)₂²¹ and its homologues.²²

Although the isolation of the anionic compound **4** supports the zwitterionic nature of **3**, (PPN)·**4** does not convert to **3** in the presence of LCuCl. The dinuclear structural integrity of **3** remains intact upon dissolution although fluxional motions become operative above 253 K since coalescence occurs at this temperature as observed by variable temperature ³¹P{¹H} FTNMR spectroscopy.^{8a} At 203 K, the two phosphorus nuclei of **3** are distinguishable while the two

CH hydrogens of the carborane cage remain indistinguishable in ^1H NMR, indicating that at least one kind of fluxional motion is still present at this temperature. The evidence at hand does not unequivocally reveal the nature of the fluxional processes.

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Supplementary Material Available: Details of crystallographic data collection, tables of positional and thermal parameters and interatomic distances and angles (15 pages). Ordering information is given on any current masthead page.

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7. a) Suitable crystals of **3** and (PPN), **4** were grown from dichloromethane/ether. Diffraction data on both compounds were collected at 25 °C on a locally built automated diffractometer, using Mo K α radiation, to a maximum 2θ of 50°. The structures were solved by a combination of conventional Patterson, Fourier and least-squares techniques.
b) Crystallographic data for **3** [(PPN)·**4**]: $a = 10.005(2)$ [11.507(1)] Å, $b = 20.693(4)$ [14.772(1)] Å, $c = 18.998(3)$ [30.751(2)] Å, $\beta = 92.664(6)$ [90.284(2)] °, $V = 3924$ [5227] Å³; space group, $P2_1/n$ [$P2_1/n$]; unique data ($I > 3 \sigma(I)$), 5071 [4831]; R (R_w), 4.5 (6.1) [6.4 (7.5)] %. All calculations were performed on the DEC VAX 750 of the J. D. McCullough Crystallography Laboratory using the UCLA Crystallography Package.
8. (a) Data for **3**: Anal. Calcd. (Found): C, 58.21 (57.94); H, 5.27 (5.10); B, 12.41 (11.79); Cu, 16.21 (16.11); P, 7.90 (7.44). IR spectrum (KBr): $\nu_{BH} = 2559, 2498$; $\nu_{BHCu} = 2327$ (weak and broad) cm⁻¹. Chemical shifts upfield of the reference are designated as negative. ¹¹B{¹H} NMR (160.463 MHz) in dichloromethane, referenced to external BF₃·OEt₂ in C₆D₆: -17.4, -19.7, -22.5, -24.2, -29.7, -31.2 ppm. ¹H NMR (200.133 MHz) in CD₂Cl₂ (referenced to residual solvent protons = 5.32 ppm): 2.01 (carborane CH). ³¹P{¹H} NMR (81.02 MHz) (CD₂Cl₂; referenced to 85% H₃PO₄): 7.9 (above 253 K); 4.7 and 10.1 ppm (at 203 K). (b) Data for **4**: Anal. Calcd. (Found): C, 67.48 (67.44); H, 5.66 (5.75); B, 9.76 (9.57); Cu, 6.37 (6.26); N, 1.41 (1.36); P, 9.32 (9.39). IR spectrum (KBr): $\nu_{BH} = 2571, 2537, 2488, 2418$ cm⁻¹. ¹¹B{¹H} NMR (CH₂Cl₂): -17.2, -20.2, -22.1, -23.0, -24.9, -34.9 ppm. ¹H NMR in CD₂Cl₂: 1.57 ppm (carborane CH). ³¹P{¹H} NMR (CD₂Cl₂): 20.6 (PPN), 7.8 (PPh₃) ppm.
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13. a) $\theta + \phi = 14.5^\circ$, $\Delta = 0.52 \text{ \AA}$ for $[\text{C}_2\text{H}_4(\text{NMe}_2)_2]\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 12c. b) $\theta = 4.7^\circ$, $\phi = 4.4^\circ$, $\Delta = 0.42 \text{ \AA}$ for $(\text{PEt}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}$. Reference 10. c) $\theta = 7.7^\circ$, $\phi = 9.5^\circ$, $\Delta = 0.5 \text{ \AA}$ for $(\text{S}_2\text{CNEt}_2)\text{AuC}_2\text{B}_9\text{H}_{11}$. Reference 11 and Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 1019.
14. The mean M-C/M-B distances ratio for the *closo* icosahedral metallocarboranes excluding the *commo* systems: a) 0.97 in $(\text{PPh}_3)_2(\text{HSO}_4)\text{RhC}_2\text{B}_9\text{H}_{11}$. Kalb, W. C.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1979**, 101, 5417. b) 0.99 in $(\text{PPh}_3)(\text{Br}_2)\text{RhC}_2\text{B}_9\text{H}_{11}$. Zheng, L.; Baker, R. T.; Knobler, C. B.; Walker, J. A.; Hawthorne, M. F. *Inorg. Chem.* **1983**, 22, 3350. c) 0.99 in $[\text{Re}(\text{CO})_3\text{C}_2\text{B}_9\text{H}_{11}]^-$. Reference 12a. d) 0.99 in $(\text{PPh}_3)_2\text{HRhC}_2\text{B}_9\text{H}_{11}$. Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Cryst.* **1976**, B32, 264. e) 1.0 in $(\text{PPh}_3)(\text{NO}_3)\text{RhC}_2\text{B}_9\text{H}_{11}$. Demidowicz, Z.; Teller R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 831. f) 1.01 in $[(\text{PPh}_3)_2\text{RhC}_2\text{B}_9\text{H}_{11}]^-$. Reference 12b. g) 1.02 in $(\text{PPh}_3)(\text{CO})\text{-RhC}_2\text{B}_9\text{H}_{10}(\text{C}_5\text{H}_5\text{N})$. Teller, R. G.; Wilczynski, J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472. h) 1.02 and 1.03 in $[(\text{PPh}_3)\text{RhC}_2\text{B}_9\text{H}_{11}]_2$. Reference 3a,b. i) 1.08 in $(\text{PMe}_3)_2\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 12c.

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Figure Captions

Figure 1. Structure of $[(PPh_3)_2Cu_2(\mu-H)_2C_2B_9H_9]$ (3) showing atom-labeling scheme. Labeling of phenyl rings and all hydrogen atoms except the bridging hydrides have been omitted for clarity. Selected values of interatomic distances (Å) and angles (deg): Cu(01)-Cu(03), 2.576(1); Cu(01)-P(02), 2.197(1); Cu(03)-P(01), 2.164(1); Cu(03)-C(C₂B₃ face), 2.331(4), 2.280(4); Cu(03)-B(C₂B₃ face), 2.226(5), 2.164(5), 2.140(5); Cu(01)-B(C₂B₃ face), 2.173(5), 2.210(4); P(01)-Cu(03)-B(10), 162.5(1).

Figure 2. Structure of $[(PPh_3)CuC_2B_9H_{11}]^-$ (4) showing atom-labeling scheme. Selected values of interatomic distances (Å) and angles (deg): Cu(03)-P(01), 2.147(2); Cu(03)-C(C₂B₃ face), 2.316(6), 2.317(6); Cu(03)-B(C₂B₃ face), 2.181(7), 2.167(7), 2.116(7); P(01)-Cu(03)-B(10), 162.9(1).

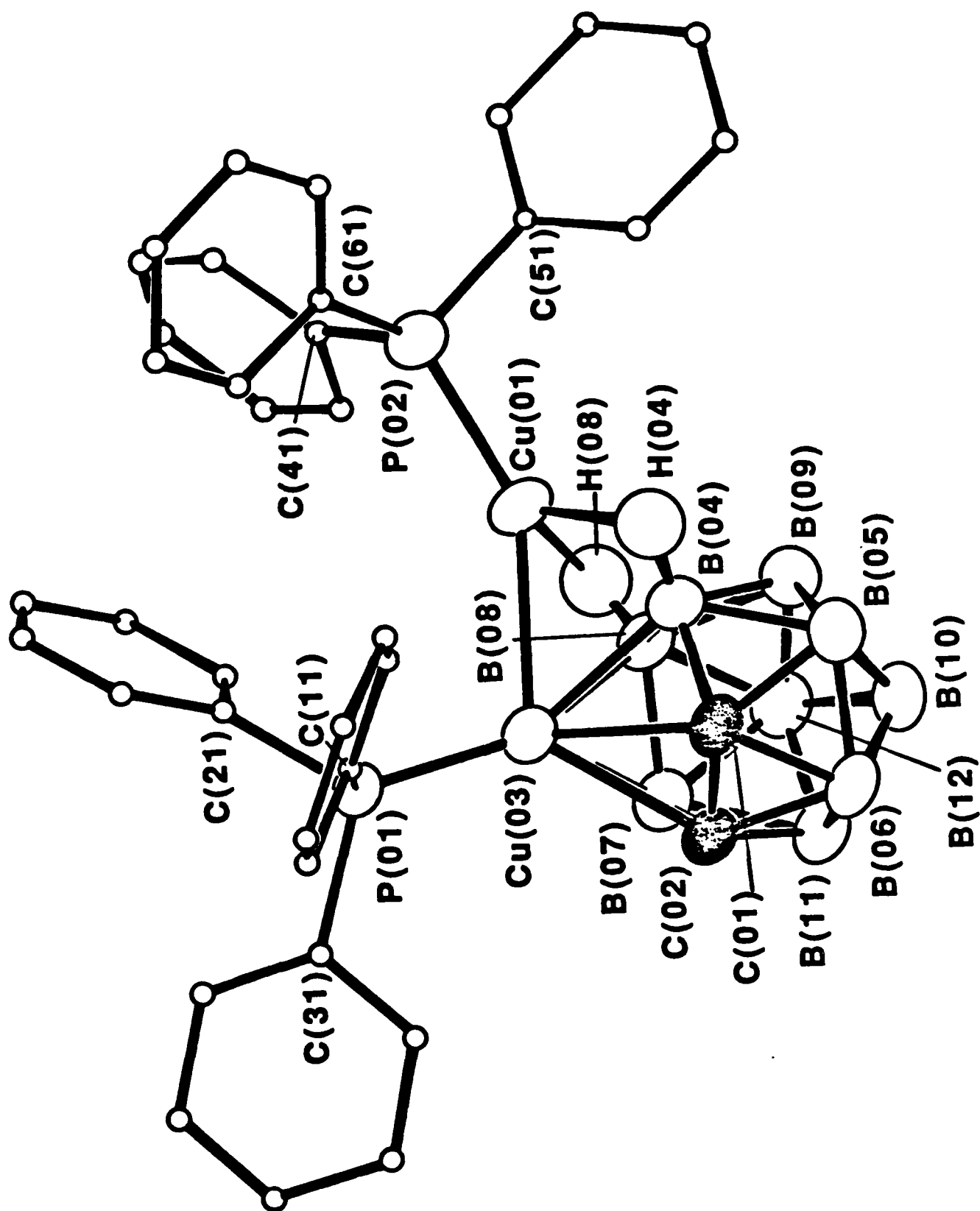
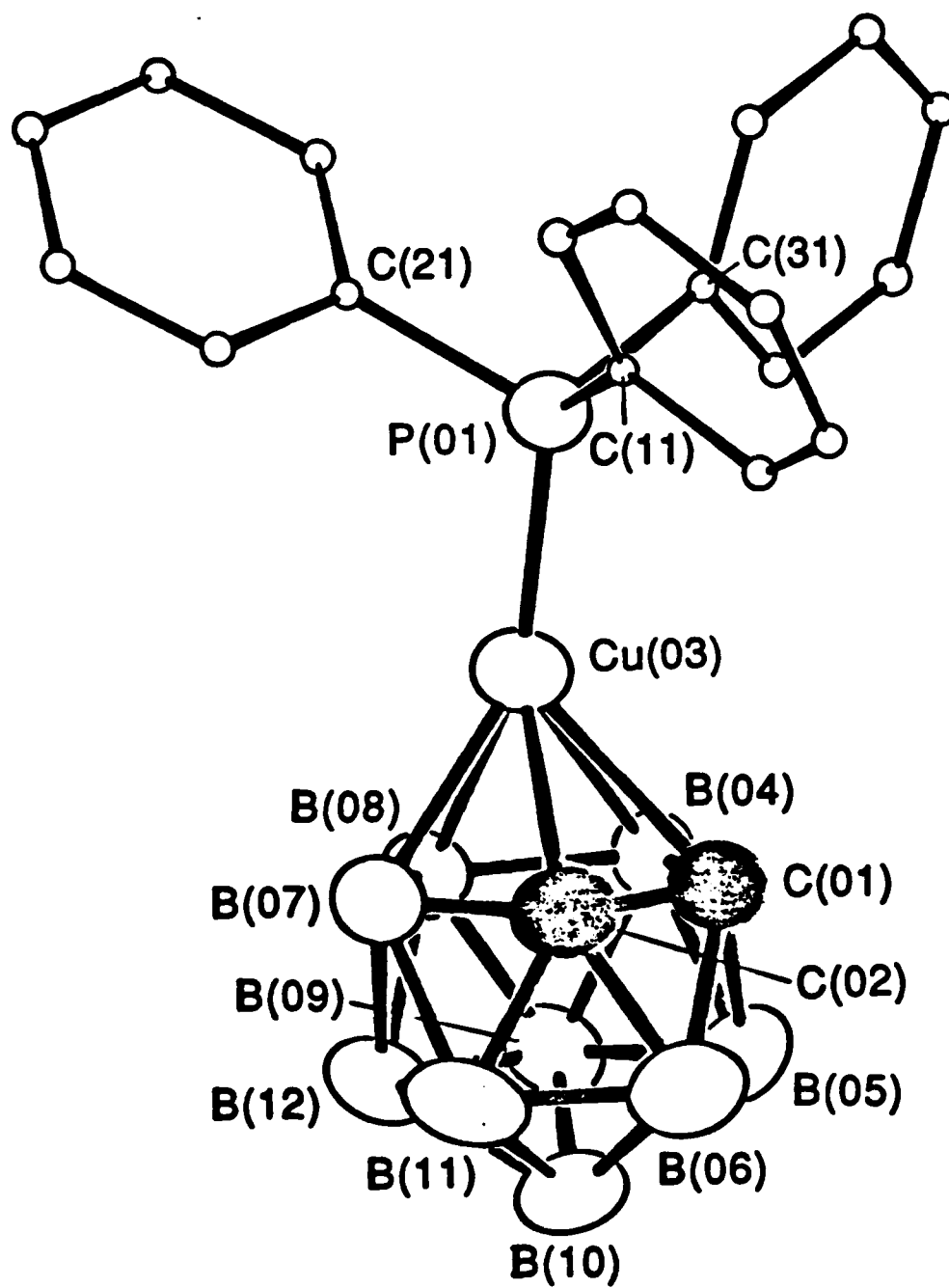


Fig #2



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